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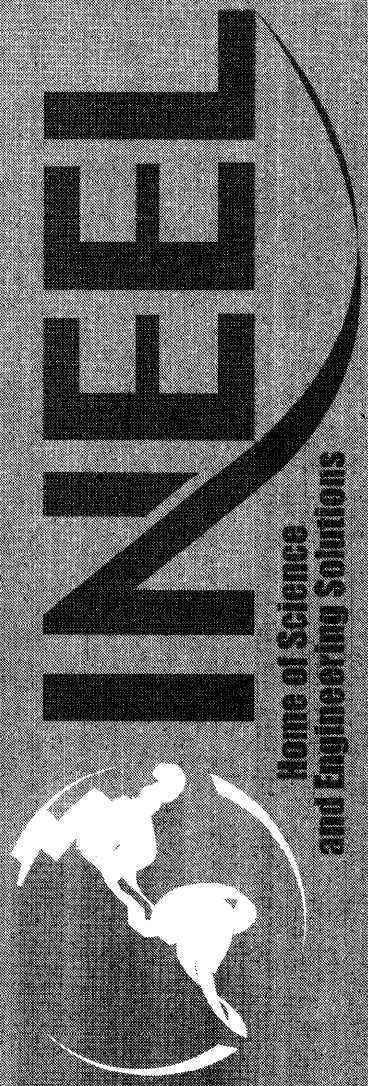

Idaho National Engineering and Environmental Laboratory
Bechtel BWXT Idaho, LLC

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Title: **ASSESSMENT OF URANIUM AND PLUTONIUM IN THE SATURATED AND UNSATURATED ZONES BENEATH THE SUBSURFACE DISPOSAL AREA, INEEL.**

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Table of Contents

0.0 Executive Summary

Twenty-two groundwater samples from beneath the Surface Disposal Area (SDA), INEEL, were investigated to determine if uranium (U) and/or plutonium (Pu) have migrated from the disposal sites into the subsurface. Groundwater samples include nine aquifer samples, 13 samples from the vadose zone including two samples from perched-water zones. One sample from the Big Lost River was also studied because it is suspected that this water is a potential source for some groundwater beneath the SDA. Each sample was filtered at 0.5 μm. The filtrate and particulate fraction were then processed separately to examine potential modes of actinide transport.

We used Isotope Dilution - Thermal Ionization Mass Spectrometry (ID-TIMS). The method can provide accurate and precise concentration and isotopic composition of U and Pu at much lower detection limits than traditional radioactivity counting techniques.

Uranium concentrations in eight of the nine-aquifer samples are between 0.9 ppb and 2.1 ppb, values that are typical for this aquifer. Sample USGS 120 has a U concentration of 4.3 ppb, a value that is twice the average for this region, but which is still within the range of values for typical groundwater. Uranium concentrations for the vadose zone and perched water samples are extremely variable with values between 0.008 ppb and 143 ppb. The high U concentrations do not appear to be related to anthropogenic input of U, but rather are likely related to natural processes in the vadose zone.

Uranium isotopic data indicate that three samples, TW1 water and filter, and 8802D water unequivocally contain anthropogenic U. Uranium in sample TW1 is enriched with a $^{238}U/^{235}U$ ratio of approximately 18 for both the water and filter samples. Uranium in sample 8802D water

is depleted with a $^{238}U/^{235}U$ ratio of 232. All three samples contain ^{236}U, which further documents the presence of anthropogenic U. Two additional samples, 8802D filter and W23L08 filter, likely contain a small component of depleted U. All other samples have natural U isotopic composition.

All samples have ^{239}Pu abundances that are near or below the detection limit for our methods and therefore none of the samples yielded unambiguous evidence for Pu. Plutonium data from two samples, TWI filter and 8802D filter, have statistically higher ^{239}Pu concentrations than the rest of the samples. It is very likely that these two samples contain ^{239}Pu at levels of approximately 5E7 atoms/sample (approximately 1.7 femtocurries/sample). Statistical tests on Pu data suggest that sample PA03 filter may contain Pu at detectable levels. The remaining samples do not contain Pu at detectable levels of approximately 5E6 atoms/sample (0.2 femtocurries/sample).

1.0 Introduction and Background

The Radioactive Waste Management Complex (RWMC) is located in the southeastern part of the Idaho National Engineering and Environmental Laboratory (INEEL, Fig. 1). The RWMC was established in 1952 as a disposal site for solid, low-level radioactive waste generated at the INEEL and other DOE sites. The Subsurface Disposal Area (SDA, Fig. 1) is a 97-acre area in the western part of the RWMC dedicated to permanent shallow-land disposal of solid, low-level waste. Transuranic waste generated by national defense programs was disposed of in the SDA from 1954 to 1970 and placed in storage from 1970 to the present. Waste was disposed in 20 pits, 58 trenches, and 21 soil vault rows. Major contaminants include organic chemicals, nitrate salts, metals, and radionuclides.

To evaluate if radionuclides have migrated into the subsurface from the SDA, INEEL contracted Los Alamos National Laboratory (LANL) to analyze groundwater samples collected from beneath the SDA for Pu and U concentration and isotopic composition by ID-TIMS. INEEL personnel and Robert Roback (LANL) collected samples during July 1999. Samples include nine aquifer waters, one sample from the Big Lost River, and 13 water samples from the vadose-zone including two perched saturated zones. Four field blanks were also taken. All samples were filtered at 0.5 μm thus splitting the sample into two aliquots: 1) the dissolved + colloidal phases (referred to as the filtrate or the dissolved phases), and 2) the particulate phases. ID-TIMS for Pu and U was conducted on the filtrate as well as the particulate fractions. Isotopic ratios presented are values corrected as described below. All uncertainties stated in this report are at the 2-sigma level.

2.0 Methods

2.1 Sample Collection

Samples were collected from wells with dedicated pumps (aquifer samples), bailing (perched water samples), or suction lysimeters by INEEL personnel using established sampling protocol (Burgess, 2000). The Big Lost River sample, BLR-99A, was collected by R. Roback at the INEEL diversion dam. All samples were collected in pre-cleaned Teflon™ bottles to minimize the potential for metals to adsorb onto the walls of the containers. In an effort to minimize the potential for air-born particulate contamination of the samples, the bottles were transported to the field in sealed plastic (zip-lock) baggies and were removed and left open for the minimum

amount of time required to receive the sample. Collection bottles were returned immediately to the zip-lock baggies, sealed, and placed in coolers for shipment to LANL.

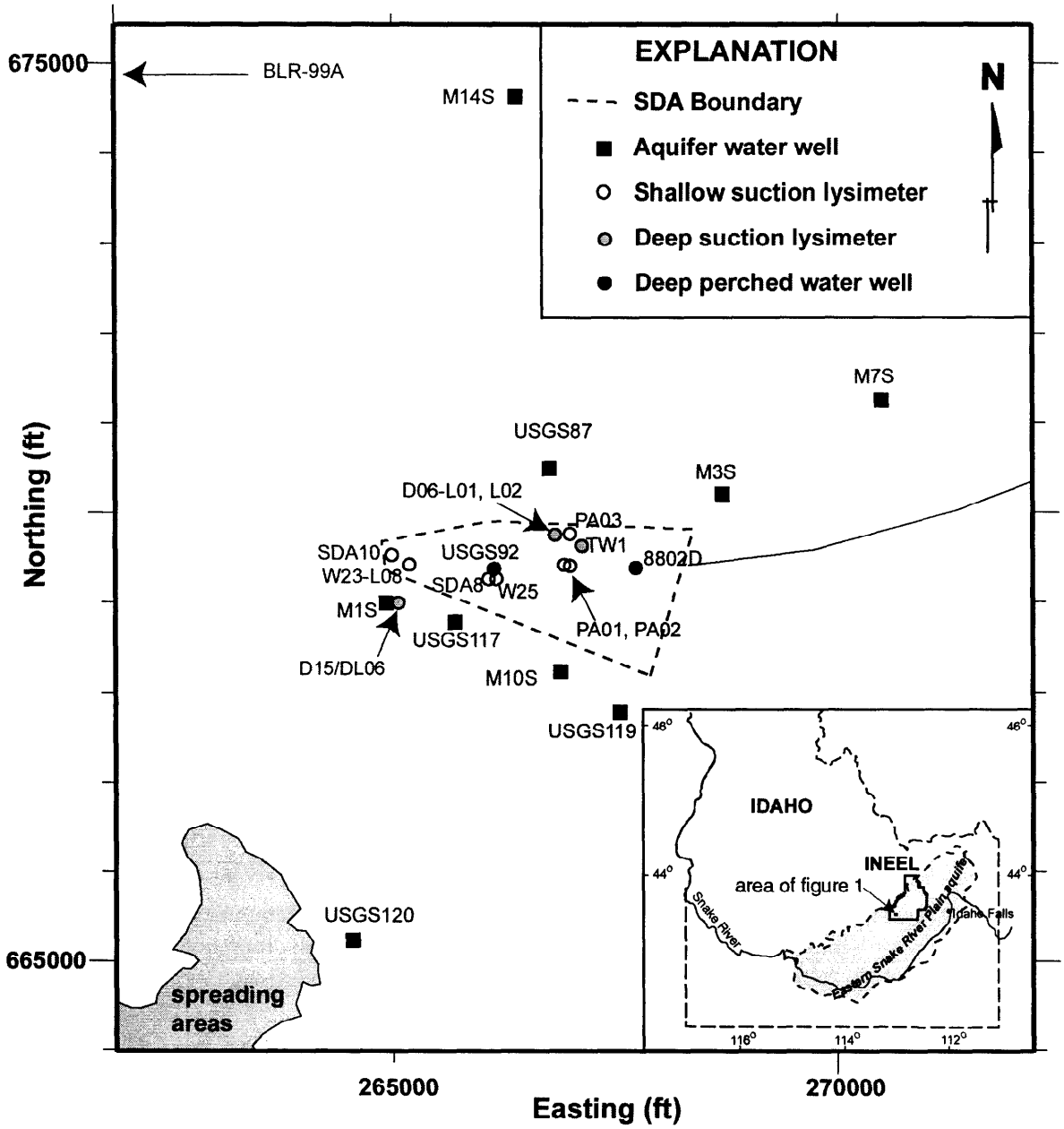

Figure 1. Maps showing locations of INEEL (inset) and of samples collected for this study. The sample of Big Lost River (BLR-99A) was collected to the west of the arrow at easting approximately 262500 ft.

Field blanks were taken at four locations within and surrounding the SDA. Field blanks consisted of ultrapure water (sub-boiling, Teflon™ distilled, 18 mega ohm water) with a known

and very low U content and no measurable Pu that were shipped to INEEL from LANL in double-bagged Teflon™ bottles. The blanks were collected by pouring the ultrapure water into another pre-cleaned Teflon™ bottle at the sampling site. The transfer time approximately equaled the amount of time needed to collect the sample; generally less than a few minutes. Field blanks were handled as samples throughout the subsequent processing and analysis.

2.2 Sample Processing

2.2.1 Filtration

All samples were weighed in the bottles before and after filtration; filtered weights were determined by difference. Samples were filtered in class 100 clean-laboratory conditions using 0.5 μm pre-cleaned Teflon™ filters. The filters were transferred to pre-cleaned Teflon™ vials for further processing (see below). The filtrate was returned to the original collection bottle after the bottle had been rinsed twice with 18 mega ohm water. All subsequent sample processing took place in either class 100 or class 10 clean-laboratory conditions.

The amount of visible particulate material collected on the filters was variable (Table 1). Approximately half of the filters showed no visible material. Of the other half, most showed only a slight yellow to brown stain. Three of the samples yielded significant material that was yellow to deep red and spongy in character and likely consisted largely of Fe-hydroxides. A small piece representing approximately 5 percent of each sample was cut from the filter using a cleaned scalpel and stored for mineralogical analysis. The mass of the particulate material was not determined; therefore, the amount of U and Pu on the filter is reported (Table 1) as the total mass and the mass per mass of water filtered.

Sample USGS 92 differed from the remaining samples in that it was quite muddy; containing approximately one-quarter sediment estimated by volume. This sample was shaken and then set aside to allow the sediment to settle. The water was then carefully decanted from the bottle to minimize resuspension of the sediment. Regardless, a significant amount of sediment was decanted to the filter. Two filters were required to filter sufficient water for analysis. The filters were dried in a clean hood and an approximately 1-gram aliquot for U and Pu analysis was removed, weighed, and processed as described below.

2.2.2 Dissolution and Chemical Separation

All dissolution and chemical separation was performed in class 100 or class 10 clean rooms at the Clean Chemistry and Mass Spectrometry Facility (TA 48, RC 45) at LANL. Ultrapure reagents produced by Seastar™ and Optima™ were used. For all samples except 8802D, the filtrate was split into separate aliquots for U and Pu analyses.

Uranium aliquots were weighed, spiked with a ^{233}U tracer, acidified with HNO_3 acid, and evaporated to dryness. The precipitated salts were redissolved in HNO_3 acid, some samples required dissolution in a nitric acid/hydrofluoric acid mixture. Uranium was purified by nitric acid, hydrochloric and/or sulfuric acid anion exchange column chemistry using BioRad™ MP-1 anion exchange resin and eluted with ultrapure water.

Plutonium aliquots were weighed, spiked with a ^{242}Pu tracer, acidified with HNO_3 and $HClO_4$ acid, and evaporated to dryness. The precipitated salts were redissolved in HNO_3 and $HClO_4$ acid, some samples required dissolution in a nitric acid/hydrofluoric acid mixture. Plutonium was purified with a series of HNO_3 and HCl acid columns and eluted with either a 1:9 mixture of

concentrated HI acid and concentrated HCl acid or with concentrated HBr acid from BioRad™ MP-1 anion exchange resin. Additional details of Pu chemical processing are given in Efurd et al., 1993.

Due to low volume collected and the low U concentration (as determined by ICP-MS, see below), U and Pu were processed together for sample 8802D. This sample was weighed and spiked with ^{233}U and ^{242}Pu tracers, acidified with HNO_3 and $HClO_4$ acid, and evaporated to dryness. The precipitated salts were redissolved in HNO_3 acid. Uranium was separated from the Pu by collecting approximately 23 column volumes of 7M HNO_3 passed through an anion exchange column. The U was purified further as above. Plutonium was eluted with a 1:9 mixture of concentrated HI/HCl acid mixture and further purified as described above.

Solids were dissolved from the Teflon™ filters by placing the filters in a 1:1 mixture of concentrated HF and concentrated HNO_3, and warmed for approximately 24 hours. The filters were removed from the solution with cleaned plastic forceps, rinsed three times with 4N HNO_3, and discarded. In all cases this treatment produced colorless filters. Subsequent processing of the filters follows the same procedure as sample 8802D described above except for samples USGS 92, which is described below, and sample M10S. Sample M10S yielded sufficient U so that it could be split into separate U and Pu aliquots. Sample M10S was then processed as the waters described above.

Solid material from sample USGS 92 was dissolved in a cleaned Teflon 100 ml beaker in a 1:1 mixture of concentrated HF and HNO_3 acid and a few ml of $HCLO_4$ acid. The sample was dried,

fumed and redissolved in 7M HNO_3. The sample was then weighed and split into separate U and Pu aliquots.

Small aliquots of the filtrate and the solid material dissolved from the filters (and USGS 92 sediment) were removed for semi-quantitative determination of U concentration by Inductively Coupled Plasma Mass Spectrometer (ICPMS) to determine appropriate mass of U spike for each sample. In all cases, the volume of sample removed represented less than 1% of the total. This initial determination of U concentration also helped to determine subsequent sample processing and mass spectrometric procedures. This 1% reduction in volume does not affect concentration data for the water samples or for USGS 92 filter, but it does reduce the total U and Pu on the rest of the filter samples by 1% or less.

2.2.3 Analytical Techniques

Mass spectrometric analyses of most U samples and Pu for sample M7S were performed on VG Sector 54 equipped with a WARP filter. Initial U concentration measurements by ICP-MS, revealed that eight of the filters contained very small amounts of U. These samples were analyzed on a modified NBS-type (12/90) mass spectrometer with ion counting capabilities.

For most analyses performed on the VG Sector 54, U was loaded onto outgassed Ta filaments configured in a triple filament assembly with a zone-refined Re center filament. For most samples, data acquisition was accomplished by cycling the smaller ^{233}U, ^{234}U, ^{235}U and ^{236}U signals onto the Daly knob while simultaneously measuring ^{238}U and ^{235}U on Faraday collectors. Each reported isotopic measurement consisted of an average of 100 ratios. Measuring both spike and unspiked NBS U960 standards regularly over the last three years assessed reproducibility.

$^{234}U/^{238}U$ are in excellent agreement for both spike and unspiked standards. The mean $^{234}U/^{238}U$ using this procedure is 54.86 ppm ± 0.03. Some samples with low U concentrations were analyzed by loading the sample onto single carburized Re filaments in a graphite slurry and collecting ratios solely in ion counting mode. Eight filter samples with the lowest U contents were analyzed on the NBS-type instrument. These samples were loaded onto Re filaments with a graphite slurry and data were collected solely in ion-counting mode. For these analyses, ratios for the more abundant masses, ^{233}U (spike mass), ^{235}U and ^{238}U were measured at temperatures between 1600 – 1680 °C. The temperature was increased to between 1680 –1740 °C to obtain sufficient signal intensity to measure the minor isotopes ^{234}U, ^{235}U, and ^{236}U. Six analyses of a 1.6 ng NBS U960 + ^{233}U -^{236}U spike mix using this data collection routine yielded a fractionation corrected mean $^{238}U/^{235}U$ of 137.61 ± 0.5% and $^{234}U/^{238}U$ of 52.70 ± 0.5%.

With the exception of sample M7S, all Pu analyses were performed using an NBS-type mass spectrometer dedicated to Pu analyses. These samples were electroplated onto Re filaments with a Pt overplate. For all samples, data were collected in ion counting mode by cycling ^{239}Pu, ^{240}Pu, ^{242}Pu, ^{242}Pu, ^{240}Pu, ^{239}Pu. Pu analysis for sample M7S was performed on the VG Sector in ion-counting mode.

TABLE 1. Uranium and Plutonium data summary. See table footnotes and text for explanation.

	Sample	Depth of well (ft)	Total Mass Filtered (g)	Filter Description	Uranium Data: Water Sample Wt (g)	[U] in sample (ppb)	(+/-) (%)[2]	U on filter (ng)[3]	U(ng) on filter/g water filtered	(+/-) (%)	238U/ 235U[4]	(+/-) (%)	236U/ 238U[5]	(+/-) (%)	234U/ 238U (ppm)	(+/-) (%)	Plutonium Data[1]: Water Sample Wt (g)	239Pu atoms in sample	(+/-) (%)	240Pu/ 239Pu	(+/-) (%)
AQUIFER SAMPLES																					
1	M1S	a6			258.45	1.230	0.63				137.95	0.32	4.2E-07	101	116.1	2.00	1739.9				
2	M1S Filter		2985	colorless				1.71	5.7E-04	5.00	137.86	0.56	-1.5E-06	951	96.1	1.69					
3	M3S	a			262.07	1.956	0.25				137.68	0.20	2.6E-08	38	122.0	0.25	1761.5				
4	M3S Filter		3053	colorless				0.802	2.6E-04	10.6	137.75	0.58	-8.5E-07	29	106.6	1.21					
5	M7S	a			264.20	1.892	0.51				137.86	0.34	1.7E-07	90	121.1	0.54	1743.8				
6	M7S Filter		2812	colorless				8.807	3.1E-03	0.89	137.51	0.28	-8.8E-08	582	121.1	1.60					
7	M10S	a			266.35	0.922	0.50				138.44	0.47	2.9E-07	83	115.9	0.49	1936.5				
8	M10S Filter		2697	deep red brown				268.6	1.0E-01	0.31	137.88	0.25	3.5E-08	30	49.0	0.38					
9	M14S	a			344.17	2.060	0.28				137.76	0.20	1.6E-07	102	120.8	0.35	1696.7				
10	M14S Filter		2974	slight yellow brown				8.24	2.8E-03	0.89	137.57	0.22	3.2E-07	51	87.5	1.22					
11	USGS 87	a			334.23	1.858	0.47				137.73	0.42	-3.2E-09	600	120.0	0.66	1650.4				
12	USGS 87 Filter		2893	slight yellow brown				4.315	1.5E-03	1.68	138.16	0.20	6.9E-07	70	118.2	1.61					
13	USGS 117	a			310.38	1.248	0.19				138.04	0.20	4.3E-08	45	117.0	0.35	1697.4				
14	USGS 117 Filter		2814	slight yellow brown				3.136	1.1E-03	2.31	137.66	0.30	1.4E-06	82	117.0	1.91					
15	USGS 119	a			323.64	1.013	0.28				137.71	0.22	8.3E-08	180	116.9	0.36	1693.5				
16	USGS 119 Filter		2942	slight yellow				1.992	6.8E-04	4.33	138.39	0.51	3.2E-07	16	100.6	0.81					
17	USGS 120	a			313.34	4.270	0.28				137.43	0.22	7.0E-08	126	108.7	0.30	1678.8				
18	USGS 120 Filter		2774	deep orange red				41.53	1.5E-02	0.56	137.37	0.25	-6.5E-09	2000	109.4	1.10					
RIVER SAMPLE																					
19	BLR-99A				326.48	2.200	0.22				137.83	0.2	4.4E-09	140	116.4	0.21	1623.6				
20	BLR-99A Filter		2642	slight brown				13.039	4.9E-03	0.58	137.64	0.2	2.9E-07	30	60.8	1.18					
VADOSE ZONE SAMPLES																					
21	PA 01	14.5			9.45	68.02	0.23				137.75	0.15	1.5E-07	8	96.0	0.22	627.40				
22	PA 01 Filter		720	colorless				0.81	1.1E-03	10.4	137.42	0.48	1.1E-06	26	98.3	1.55					
23	PA 02	8.5			9.55	46.29	0.28				137.87	0.21	7.9E-08	15	111.1	0.30	490.90				
24	PA 02 Filter		581	colorless				0.294	5.1E-04	29	138.30	0.74	1.6E-06	21	111.2	1.53					
25	PA 03	9.5			8.95	128.2	0.27				137.60	0.20	7.3E-08	14	78.2	0.34	222.96				
26	PA 03 Filter		290	colorless				7.97	2.7E-02	1	138.06	0.23	1.0E-06	31	78.9	2.52		9.8E+06	3.6E+06		
27	W23L08	12			10.71	123.9	0.35				137.28	0.30	2.8E-08	14	97.1	0.36	312.66				
28	W23L08 Filter		400	colorless				12.441	3.1E-02	0.62	**139.33**	0.20	1.6E-07	66	96.0	0.96					
29	D06L01	88			9.74	134.9	0.38				137.77	0.33	2.2E-08	40	111.9	0.41	338.83				
30	D06L01 Filter		409	very slight brown				15.8	3.9E-02	0.53	137.79	0.09	2.3E-07	32	110.0	0.67					
31	D06L02	44			5.21	143.6	0.27				138.03	0.20	1.2E-08	88	98.0	0.29	17.99				
32	D06L02 Filter		24	colorless				23.926	1.0E+00	0.4	137.62	0.20	-5.1E-07	94	98.1	1.40					
33	SDA 8	17			70.09	7.900	0.27				138.03	0.20	5.9E-08	20	95.9	0.30	246.56				
34	SDA 8 Filter		423	colorless				0.185	4.4E-04	46	136.53	1.02	4.4E-07	23	95.9	6.35					
35	SDA 10	10.5			15.15	30.24	0.31				137.27	0.30	2.4E-08	48	90.5	0.35	489.82				
36	SDA 10 Filter		578	colorless				0.877	1.5E-03	9.7	138.84	0.80	-6.4E-08	25	91.0	2.35					
37	TW 1	102			18.69	28.90	0.18				**17.63**	0.03	**2.11E-04**	0.18	**612**	0.10	256.09				
38	TW 1 Filter		321	very slight brown				2.944	9.2E-03	2.44	**18.13**	2.20	**2.07E-04**	3.3	**597**	2.40		5.1E+07	1.1E+07	0.17	82
39	D15DL06	98			98.73	2.200	0.3				137.66	0.25	2.6E-08	58	139.1	0.31	230.59				
40	D15DL06 Filter		397	slight yellow brown				2.84	7.2E-03	2.53	137.77	0.29	1.5E-06	68	139.0	1.98					
41	W25	12			65.28	9.901	0.38				137.97	0.32	1.2E-07	18	78.5	0.51	275.94				
42	W25 Filter		497	colorless				0.043	8.7E-05	198	135.54	3.50	2.7E-06	20	119.5	18.00					
PERCHED WATER SAMPLES																					
43	USGS 92	220			59.98	7.077	0.31				137.94	0.25	1.8E-07	8	89.96	0.34	93.95				
44	USGS 92 Filter[7]		214	muddy sample	0.4818	2171.8	0.27				137.78	0.19	3.2E-07	8	53.5	0.36	0.5656				
45	8802D	220			66.38	0.0079	0.76				**232.35**	1.39	**4.4E-05**	30	**47.15**	17	66.38				
46	8802D Filter		67	deep red brown				15.503	2.3E-01	0.52	**138.60**	0.15	**5.2E-07**	78	83.41	1.31		4.9E+07	6.5E+06	0.05	120

[1] Plutonium data presented here are only for samples with likely or possible ^{239}Pu detections. Table 2 presents data for all samples.

[2] All uncertainties are given at the 2-sigma level.

[3] Represents approximately 95% of the total because a portion was removed for mineralogical analysis. For sample M10S, the amount represents 48% of total because sample was split into separate U and Pu aliquots.

[4] Uranium isotopic ratios that are interpreted to include a component of anthropogenic uranium are bolded and discussed in the text.

[5] Only the four bolded results are considered above background, or possibly above background. See text for discussion.

[6] Depth to the aquifer for these wells is approximately 690 ft below land surface.

[7] USGS 92 contained a large amount of sediment. The filtered sediment was dried and weighed, weights are given for the dry sediment. This is the only filter sample that was weighed.

2.2.4 Data Reduction

Uranium concentration and isotopic data are summarized in Table 1. Uranium isotopic data were corrected for mass fractionation. The fractionation factors were determined from repeated runs of the NBS U960 standard, which mimicked run conditions of the samples. For analyses performed on the VG Sector 54, a fractionation factor of 0.05%/atomic mass unit (AMU) was applied. For U analyses performed on the NBS-type instrument a fractionation factor of 0.2%/AMU was applied to the $^{233}U/^{235}U$ and $^{233}U/^{238}U$ ratios collected during the lower temperature data collection. For the higher temperature collection of $^{234}U/^{235}U$ and $^{236}U/^{235}U$ data, zero fractionation correction was applied. Uranium data were also corrected for spike and blank contribution. Blanks for processing of water samples, including the field blanks, averaged 0.04 pico moles (9.5 pico grams), a value that is in good agreement with long-term laboratory U procedural blanks. Filtration added an additional 0.65 pico moles (155 pico grams) of U blank to the sample. All water samples and most of the filter samples yielded sufficient U so that the spike and blank corrections are insignificant. However, for the few filter samples that yielded little U, these corrections are important. In particular, for the eight filters that yielded less than 2 nano grams of total U (Table 1) corrections to the concentration isotopic data become important. Uncertainties for the U blank correction are estimated at 50%. Propagation of these uncertainties results in greatly elevated overall errors for samples with low U yields.

Plutonium data were corrected using an in-house program written by Clarence Duffy of LANL (CST-11). Table 1 presents a summary of the data for those samples in which ^{239}Pu may have been detected. For all of the samples, the raw ^{239}Pu and ^{240}Pu instrument signals were extremely low, in all cases less than a few counts per second. Given such low instrument signals, it is crucial to separate signal due to Pu atoms from other compounds that may form isobaric

interferences. Isobaric interferences will typically ionize with different efficiency than true Pu signals. Therefore the relative contribution of isobaric interference to a low Pu signal commonly changes throughout the run, resulting in changing ^{239}Pu and ^{240}Pu abundances when compared to the relatively large signal of the spike mass ^{242}Pu. The program written by C. Duffy processes raw count data, examines the changing effects of isobaric interferences through the course of the analysis, and extrapolates these changes to an infinite time to arrive at the final isotopic ratio. Plutonium data for all samples and results of statistical processing are given in table 2.

Table 2, gives the blank corrected ^{239}Pu abundance. For this study 13 blanks, including field blanks, were evaluated. With two exceptions, they are statistically equal to most of the true samples indicating that the measured values are due to interferences that are shared by samples and blanks. The blank correction and uncertainty were derived from the weighted mean of the blanks and samples that form the statistical bulk of the samples. For this analysis, the weighted mean of analyses 11-55, Table 2 was used. The weighted uncertainty of these analyses was propagated along with counting statistics to arrive at the total uncertainty for the ^{239}Pu abundance.

TABLE 2. Plutonium data for all samples and summary of statistical tests. See text and notes for explanation.

	Sample[1]	239 Pu atoms, blank corrected	2 Sigma
1	**TWI FILT**	**5.13E+07**	1.1E+07
2	**8802D FILT**	**4.87E+07**	6.5E+06
3	**PA02 FILT**	**1.16E+07**	5.5E+06
4	**PA03 FILT**	**9.83E+06**	3.6E+06
5	**SDA8 FILT**	**8.12E+06**	4.1E+06
6	**W23L08 FILT**	**7.70E+06**	6.3E+06
7	M1S FILT	4.13E+06	1.9E+06
8	M14S FILT	3.92E+06	5.5E+06
9	USGS 119 FILT	3.70E+06	1.9E+06
10	SDA08	2.76E+06	1.7E+06
11	USGS 87 FILT	2.74E+06	5.2E+06
12	USGS 120 SOLIDS	2.63E+06	5.5E+06
13	USGS 120 FILT	2.32E+06	1.6E+06
14	D06/DL02 FILT	2.05E+06	6.4E+06
15	D06/DL01 FILT	1.35E+06	1.1E+07
16	BLR 99A FILT	1.32E+06	6.1E+06
17	SDA10	1.28E+06	2.7E+06
18	TWI	1.09E+06	3.3E+06
19	PA03	1.01E+06	1.5E+06
20	USGS 92 FILT	8.89E+05	1.2E+07
21	PA01 FILT	7.03E+05	6.7E+06
22	D06DL01	5.86E+05	1.9E+06
23	USGS 120	5.73E+05	6.3E+05
24	USGS 119	4.77E+05	2.5E+06
25	*Field Blank 7-28-99 11:20*	4.57E+05	1.2E+06
26	USGS 87	2.45E+05	6.2E+06
27	PA02	4.34E+04	2.3E+06
28	D06DL02	-3.48E+04	5.9E+06
29	*Filtration Blank*	-1.70E+05	1.4E+06
30	M3S FILT	-2.29E+05	3.8E+06
31	USGS 92	-4.10E+05	3.3E+06
32	*BLANK 5*	-4.38E+05	1.1E+06
33	M7S FILT	-4.39E+05	2.2E+06
34	USGS 117 FILT	-4.39E+05	2.6E+06
35	M10S FILT	-5.17E+05	5.7E+06
36	W25 FILT	-5.46E+05	1.4E+06
37	D15DL06 FILT	-7.05E+05	3.3E+06
38	*Field Blank 7-28-99 9:30*	-7.33E+05	1.2E+06
39	*BLANK 3*	-7.61E+05	1.2E+06
40	PA01	-9.26E+05	3.7E+06
41	M14S	-9.42E+05	8.1E+06
42	USGS 119 SOLIDS	-1.08E+06	1.3E+06
43	*FILTER H20 BLANK*	-1.18E+06	3.7E+06
44	W25	-1.18E+06	1.8E+06
45	*D3-H20 BLANK*	-1.31E+06	1.1E+07
46	D06L01 SOLIDS	-1.40E+06	4.4E+06
47	8802 D	-1.59E+06	5.7E+06
48	SDA10 FILT	-1.93E+06	5.3E+06
49	D15-DL06	-2.08E+06	4.8E+06
50	*BLANK 4*	-2.53E+06	7.3E+06
51	BLR 99A	-2.78E+06	6.1E+06
52	*BLANK 6*	-3.30E+06	4.0E+06
53	*M10S Field Blank*	-3.48E+06	8.5E+06
54	*M7S Field Blank*	-4.44E+06	4.7E+06
55	M3S	-5.63E+06	5.9E+06
56	*BLANK 2*	-1.26E+07	9.1E+06
57	W23 L08	-1.81E+07	1.8E+07
58	*BLANK 1*	-9.46E+07	2.3E+07

	Sample[1]	Inverse of the Normal Cumulative Distribution
1	**TWI FILT**	**0.012**
2	**8802D FILT**	**0.080**
3	**PA02 FILT**	**0.124**
4	**PA03 FILT**	**0.157**
5	**SDA8 FILT**	**0.184**
6	**W23L08 FILT**	**0.207**
7	M1S FILT	0.228
8	M14S FILT	0.247
9	USGS 119 FILT	0.264
10	SDA08	0.280
11	USGS 87 FILT	0.295
12	USGS 120 SOLIDS	0.309
13	USGS 120 FILT	0.323
14	D06DL02 FILT	0.336
15	D06DL01 FILT	0.348
16	BLR 99A FILT	0.360
17	SDA10	0.371
18	TWI	0.383
19	PA03	0.394
20	USGS 92 FILT	0.404
21	PA 01FILT	0.415
22	D06DL01	0.425
23	USGS 120	0.436
24	USGS 119	0.446
25	*Field Blank 7-28-99 11:20*	0.456
26	USGS 87	0.466
27	PA02	0.476
28	D06DL02	0.485
29	*Filtration Blank*	0.495
30	M3S FILT	0.505
31	USGS 92	0.515
32	*BLANK 5*	0.524
33	M7S FILT	0.534
34	USGS 117 FILT	0.544
35	M10S FILT	0.554
36	W25 FILT	0.564
37	D15DL06 FILT	0.575
38	*Field Blank 7-28-99 9:30*	0.585
39	*BLANK 3*	0.596
40	PA01	0.606
41	M14S	0.617
42	USGS 119 SOLIDS	0.629
43	*FILTER H20 BLANK*	0.640
44	W25	0.652
45	*D3-H20 BLANK*	0.664
46	D06L01 SOLIDS	0.677
47	8802 D	0.691
48	SDA10 FILT	0.705
49	D15-DL06	0.720
50	*BLANK 4*	0.736
51	BLR 99A	0.753
52	*BLANK 6*	0.772
53	*M10S Field Blank*	0.793
54	*M7S Field Blank*	0.816
55	M3S	0.843
56	*BLANK 2*	0.876
57	W23 L08	0.920
58	*BLANK 1*	0.988

	Sample[1]	# of Occurrences Expected[2]
1	**8802D FILT**	**2.32E-12**
2	**TWI FILT**	**1.31E-04**
3	***BLANK 1***	**8.54E-04**
4	**PA03 FILT**	**1.65E-01**
5	M1S FILT	8.26E-01
6	PA02 FILT	1.01E+00
7	SDA8 FILT	1.40E+00
8	USGS 119 FILT	1.62E+00
9	SDA08	2.74E+00
10	USGS 120 FILT	4.28E+00
11	*BLANK 2*	4.78E+00
12	W23L08 FILT	6.40E+00
13	W23L08	9.50E+00
14	M3S	9.90E+00
15	*M7S FIELD BLANK*	9.96E+00
16	USGS 120	1.05E+01
17	USGS 119 SOLIDS	1.14E+01
18	*EFURD BLANK 6*	1.17E+01
19	M14S FILT	1.39E+01
20	PA03	1.44E+01
21	W25	1.50E+01
22	*BLANK 3*	1.54E+01
23	*Field Blank 7-28-99 9:30*	1.57E+01
24	USGS 87 FILT	1.74E+01
25	USGS 120 SOLIDS	1.84E+01
26	SDA10	1.84E+01
27	BLR 99A	1.89E+01
28	D15DL06	1.92E+01
29	*M10S FIELD BLANK*	1.98E+01
30	W25 FILT	2.00E+01
31	*BLANK 5*	2.02E+01
32	*Field Blank 7-28-99 11:20*	2.02E+01
33	SDA10 FILT	2.08E+01
34	*BLANK 4*	2.11E+01
35	TWI	2.16E+01
36	*FILTER H20 BLANK*	2.18E+01
37	D06DL02 FILT	2.17E+01
38	D06L01 SOLIDS	2.18E+01
39	D06DL01	2.21E+01
40	8802 D	2.26E+01
41	PA01	2.33E+01
42	BLR 99A FILT	2.40E+01
43	D15DL06 FILT	2.41E+01
44	M7S FILT	2.44E+01
45	USGS 119	2.46E+01
46	USGS 117 FILT	2.51E+01
47	USGS 92	2.61E+01
48	D06/DL01 FILT	2.62E+01
49	*Filtration Blank*	2.62E+01
50	*D3-H20 BLANK*	2.62E+01
51	M14S	2.63E+01
52	PA 01 FILT	2.66E+01
53	M10S FILT	2.69E+01
54	USGS 92 FILT	2.72E+01
55	M3S FILT	2.76E+01
56	USGS 87	2.81E+01
57	PA02	2.86E+01
58	D06DL02	2.89E+01

[1] Filt = Filter. [2] See text for explanation. Samples bolded are discussed in text regarding the possibility that they may vary statistically from the remainder of the data set. Blanks are italicized, unless otherwise noted all blanks are total procedural. D3-H20 refers to teflon distilled water.

Solids refers to the fraction of a sample that remained solid after treatment with heated 7M $HN0_3$ acid. These were separated from the acid and dissolved with more vigorous acid treatments. The two aliquots were then processed separately to evaluate Pu partitioning between the solution and the solids.

3.0 Results

3.1 Uranium

All natural samples contain U at some level. Dissolved U concentration in groundwater is typically in the parts per billion (ppb) range (Osmond and Cowart, 1992). INEEL aquifer samples have U concentrations ranging from 0.3 to 3.6 ppb with most samples containing between 1 and 2 ppb (Knobel et al., 1991, Roback et al., in review). This project is the first (to the authors' knowledge) to obtain high-accuracy U isotopic measurements for INEEL vadose-zone samples. Natural U has a $^{238}U/^{235}U$ atomic ratio of 137.88 and contains no ^{236}U (Walker et al, 1989). The $^{234}U/^{238}U$ ratio in nature varies. The $^{234}U/^{238}U$ ratio is approximately 0.000055 (55 ppm) when the ^{234}U is in secular equilibrium with ^{238}U. In most groundwaters, ^{234}U is enriched relative to ^{238}U. Typical $^{234}U/^{238}U$ ratios for INEEL groundwater range from 0.000086 to 0.000166 (Roback, et al., in review). Results of U analyses for this study are presented in Table 1 and summarized graphically in Figures 1, 2, and 3.

3.1.1 Uranium Concentration

All but one of the aquifer samples has U concentrations between 0.9 and 2.1 ppb, values that are typical for groundwater at INEEL (Roback et al., in review) and for oxygenated waters globally (Osmond and Cowart, 1992). The only aquifer sample that falls outside of this range is USGS 120, which has a value of 4.3 ppb. This value is the highest known U concentration in parts of the Snake River Plain aquifer in the vicinity of the INEEL *and* away from sources of potential contamination of approximately 73 aquifer samples measured to date (Roback, et al., in review and this report). Although this value is anomalously high for the INEEL region, it is still within the expected range of U concentration for oxygenated groundwater (Osmond and Cowart, 1992).

Uranium concentration of Big Lost River water is 2.2 ppb in close agreement to the value of 2.4 ppb measured previously (Roback, et al., in review).

Uranium concentrations of vadose zone and perched water samples are quite variable with values ranging between 0.008 ppb to 143.6 ppb. With two exceptions, these values are considerably higher than those of the aquifer samples. These high U concentrations likely reflect the greater availability of exchangeable and/or dissolvable uranium in the surficial alluvium relative to the basalt aquifer or the lower water to rock ratios of the vadose zone when compared to the saturated zone or a combination of both. The lower values, and in particular the extremely low value of 0.008 ppb for 8802D, may reflect anomalous reducing conditions. The possibility of such reducing conditions invites the question that they may be caused by leaking of leachates into this sampling site. Additional geochemical studies are needed to address this issue.

The amount of U collected on the filters is also quite variable with values ranging from 0.00009 ng U/g water filtered to 1.0 ng U/g water filtered. The amount of U collected by filtration does not show a consistent correlation among sample types. For example, the amount of U collected on the filters for the aquifer samples vary by over three orders of magnitude, the vadose zone samples encompass the entire range of values. The filtered material for sample USGS 92 has a U concentration of 2172 ppb (2.172 ppm) a value that is typical for common rocks (Faure, 1986).

3.1.2 Uranium Isotopic Ratios

Figures 2-4 show plots of the U isotopic ratios and 2-sigma uncertainties for all of the samples. Nine of the samples plot off of the "natural U" line on a plot of $^{238}U/^{235}U$ ratios (Fig. 2) at the 2-sigma level of uncertainty. Three of the samples, TW1 water and filter and 8802D water, plot

well away from the remainder of the samples. In the following, TW1 and 8802D are discussed first, followed by the samples that plot only slightly off of the natural U line. The samples for which natural U isotopics were determined are discussed last.

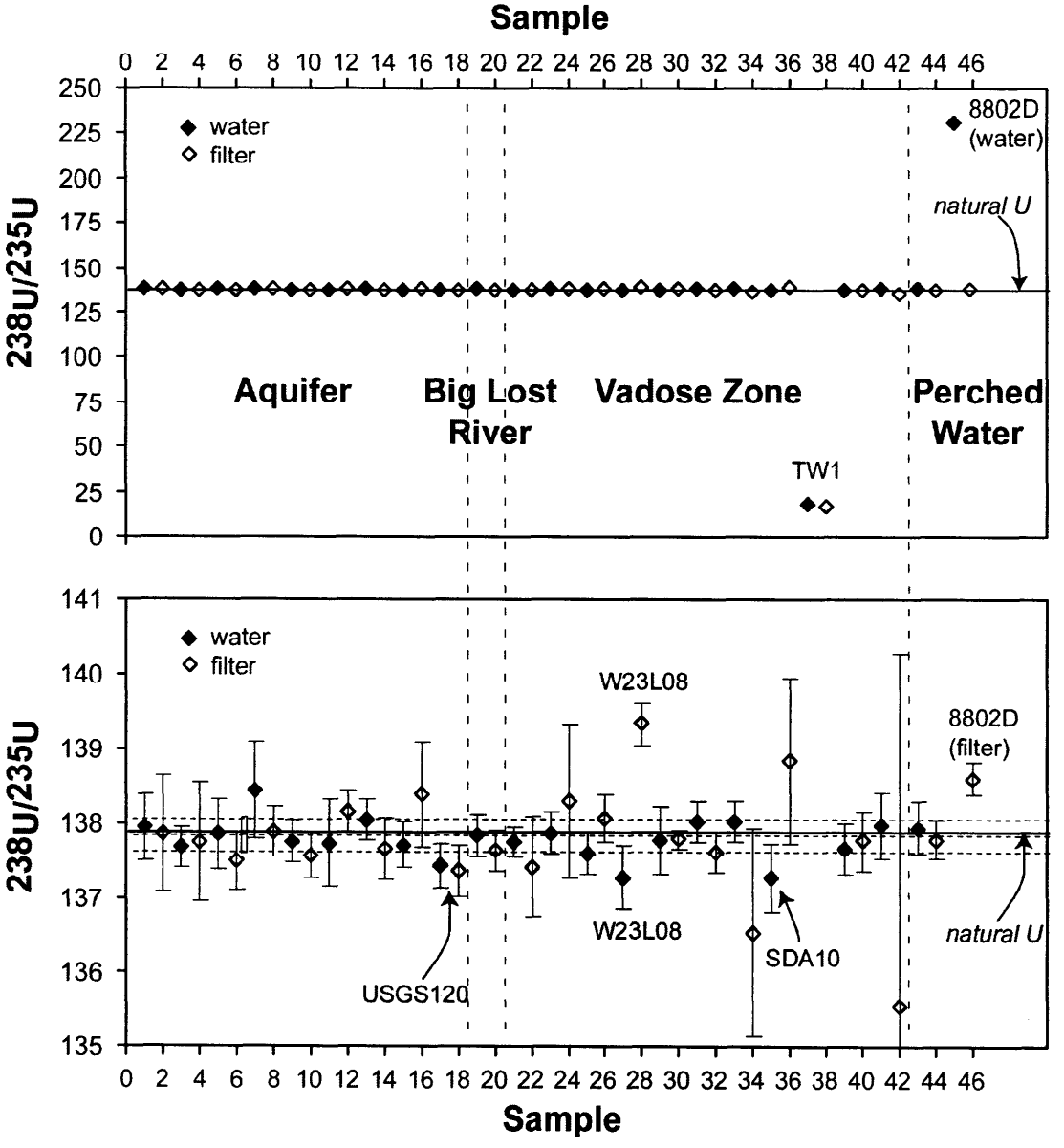

Figure 2. Plot of $^{238}U/^{235}U$ ratios and two-sigma error bars. Upper plot shows all samples; the lower plot is at a greatly expanded scale to facilitate examination of the bulk of the samples, which plot on or near the $^{238}U/^{235}U$ ratio of natural U. Dashed lines are mean and ± one standard deviation of reference samples (see text for discussion). Samples labeled are discussed in the text. Sample number identifiers are keyed to Table 1.

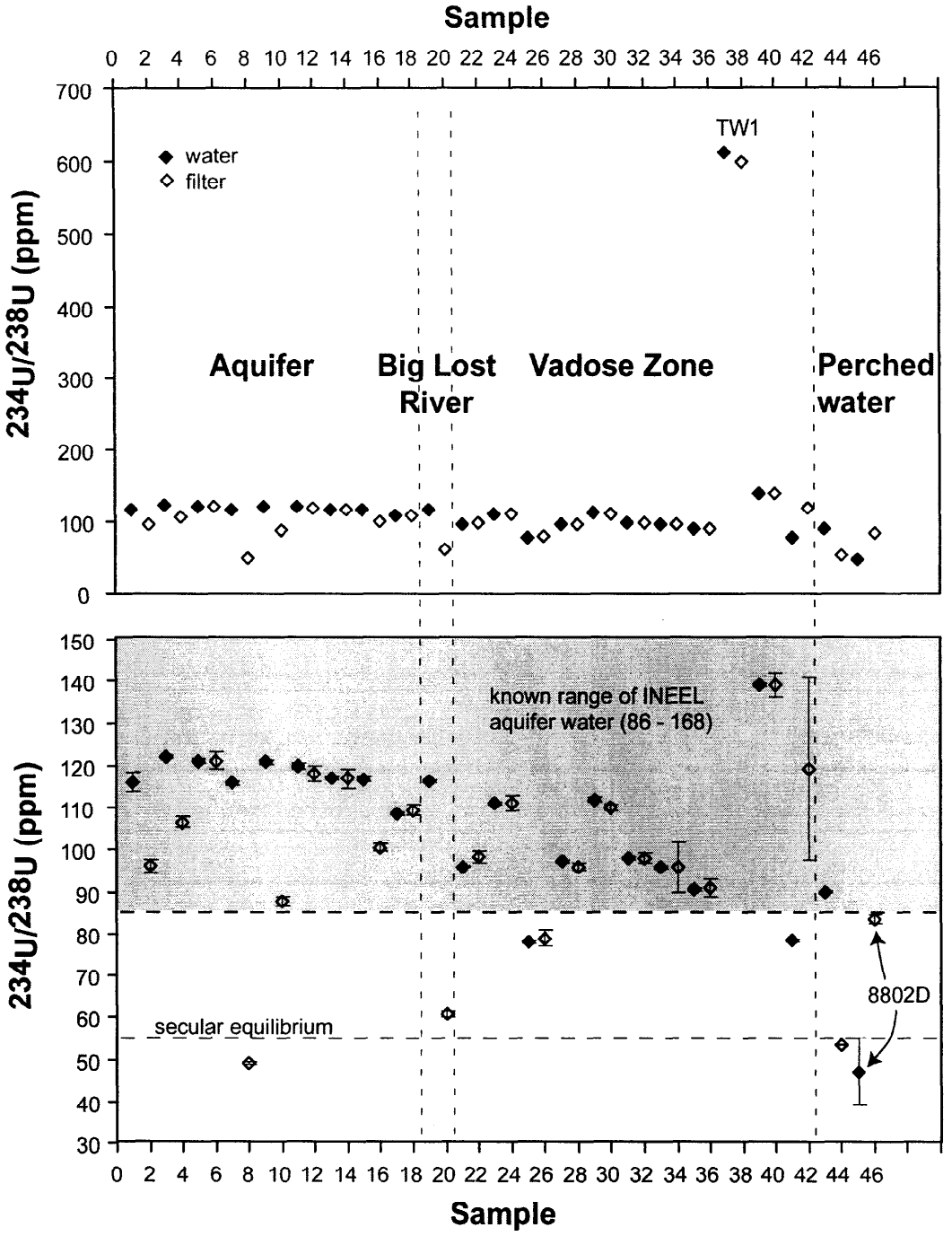

Figure 3. Plot of $^{234}U/^{238}U$ ratios and two-sigma error bars. Upper plot shows all samples; the lower plot is at a greatly expanded scale to facilitate examination of the bulk of the samples. Samples labeled are discussed in the text. Also shown on the plot are $^{234}U/^{238}U$ ratios for secular equilibrium and the range of known values for aquifer samples near INEEL (from Roback et al., in review). Sample number identifiers are keyed to Table 1. See text for discussion.

Approximately 19 grams of water were analyzed from TW1. The U concentration of the sample is about 29 ppb a value that is within the range of concentrations of the other vadose-zone samples. The $^{238}U/^{235}U$ of the sample is 17.63 ±0.03%, clearly indicating that the sample contains a significant percentage of enriched U. The $^{236}U/^{238}U$ ratio is 0.000211 ±0.18%, unequivocally indicating the presence of ^{236}U. The calculated amount of ^{236}U present is 1.6E10 atoms of ^{236}U per gram of sample. The $^{234}U/^{238}U$ of the sample is 0.000612 ±0.10% a value that is anomalously high for all INEEL samples analyzed for this study. Although the $^{234}U/^{238}U$ ratio does not prove anthropogenic input, it is likely that the elevated ^{234}U is due to addition of enriched U. Particulates filtered from this sample carried 2.94 ng of U, which also have non-natural isotopics. The $^{238}U/^{235}U$ of the particulate material is 18.13 ± 2.2%, the $^{236}U/^{238}U$ ratio is 0.000207 ±3.3%, and the $^{234}U/^{238}U$ of the sample is 0.000597 ± 2.4%. All of these values are in good agreement with the isotopic ratios from the water sample. These data clearly indicate that anthropogenic U is present in both the particulate fraction and the dissolved or colloidal fractions of this sample.

Approximately 66 grams of water from the perched water at 8802D were analyzed. The U concentration of the sample is about 0.0079 ppb, a value that is the lowest observed for this sample set and, in fact, for all INEEL water analyses performed by the author to date. The $^{238}U/^{235}U$ of the sample is 231.1 ± 1.4%, clearly indicating that the sample contains a significant percentage of depleted U. The $^{236}U/^{238}U$ ratio is 0.000044 ± 30%, unequivocally indicating the presence of ^{236}U. The calculated amount of ^{236}U present is 8.9E5 atoms of ^{236}U per gram of sample. The $^{234}U/^{238}U$ of the sample is 0.000047 ± 17%. Due to the high uncertainty of this analysis, this value overlaps with U in secular equilibrium; however, the value is probably low due to the presence of depleted U (see below).